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**REMARKS**

Initially, applicants would like to thank the Examiner, Ms. Tran, for the courteous and helpful interview extended to their undersigned attorney on March 12, 2004. The claims have been amended in light of the results of the interview. The substance of the interview is reflected in the following remarks.

Claim 7 has been amended as proposed during the interview to recite that the adsorbent zone and catalyst zone are provided --in an in-line exhaust pipe-- as opposed to the prior recitation of the adsorbent zone and catalyst zone being provided "in-line in an exhaust pipe." This amendment is based on the description on page 11, lines 10-14, of the application. A new independent claim, claim 29, and a new dependent claim, claim 30, have been added to the application. Claim 29 corresponds to amended claim 7 but recites that the adsorbent contains an H/ $\beta$ -zeolite having an SiO<sub>2</sub>/AlO<sub>3</sub> ratio of 200 or more. Claim 30 depends on claim 29 and limits the noble contained in the adsorbent (i.e., adsorbent-catalyst) to Pd. Claims 9 and 10, which included the limitations now recited in claims 29 and 30 have been cancelled. Claims 27 and 28 have also been cancelled.

Referring to the Action, the 35 U.S.C. § 112, first and second paragraph, rejections of claims 27 and 28 have been rendered moot by the cancellation of these claims.

Regarding the 35 U.S.C. § 103(a) rejections, and, first, the rejection of claims 7-22 and 26 based on the disclosure of WO 94/11623 as the primary reference, claim 7, in addition to reciting the system for exhaust gas purification of the present invention as "consisting essentially of" an adsorbent zone and a catalyst zone, now recites that the adsorbent zone and the catalyst zone are provided in an in-line exhaust pipe of an internal combustion engine with the adsorbent zone being upstream of said catalyst zone with respect to flow of said exhaust gas.

Claim 7 as amended distinguishes over WO 94/11623 because the first and second catalyst zone and the adsorbent zone of the exhaust system of WO 94/11623 are not provided in an in-line type of exhaust pipe. In an in-line exhaust pipe, the components are provided in essentially a straight line. (See the enclosed copies of SAE Technical Paper Series 970266, 980423 and 1999-01-1230). On the other hand, the exhaust system of WO 94/11623, as shown in the drawings, is a looped system in which the exhaust gas is returned to a heat exchanger (Fig. 1) or uses a cross monolith wherein a first and second catalyst zone are provided (Figs. 2-4).

For this reason alone, WO 94/11623, taken alone or in combination with the secondary references identified in the Action, cannot support a case of *prima facie* obviousness of the claims.

Referring to the 35 U.S.C. § 103(a) rejection of claims 7-22 and 26-28 over EP 661,098 ("EP '098") in view of WO 94/11623, the references are insufficient to support a case of *prima facie* obviousness. The position of the Office is that it would be obvious for a person of ordinary skill in the art to have used an H/beta-zeolite of WO 94/11623 having an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio ("SAR") of 100 or more as the adsorbent in the adsorbent-catalyst disclosed in EP '098. However, obviousness requires, first, that the prior art teach or suggest or otherwise provide a motive for making the proposed modification and, second, that the art-skilled person be able to reasonably predict that the proposed modification will be successful. Both the suggestion or motive and the reasonable expectation of success are required and have not been shown by the Office to be supported in the prior art.

There is no teaching or suggestion in EP 661,098 and/or WO 94/11623 to make the proposed modification and a motive to make the proposed modification cannot exist because of the different nature of the exhaust systems disclosed in the respective references.

Thus, the first requirement for supporting the 35 U.S.C. § 103(a) rejection is absent.

Also, the art-skilled person could not have reasonably predicted the results of using an H/beta-zeolite having an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio ("SAR") of 100 or more (as recited in claim 7) or an H/beta-zeolite having an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio ("SAR") of 200 or more (as recited in claim 29) as the adsorbent in the adsorbent-catalyst disclosed in EP '098 because the only zeolite used in the examples of the adsorbent-catalysts of EP '098 is ZSM-5. Nothing is described in EP '098 concerning the expected results of using an H/beta-zeolite as the adsorbent of the adsorbent-catalyst. WO 94/11623 discloses nothing concerning the use of any of the adsorbents described therein as the adsorbent of an adsorbent-catalyst as disclosed in EP '098 and thus provides no basis for predicting the results of using an H/beta-zeolite as the adsorbent of the adsorbent-catalyst of EP '098.

Additionally, the properties of an exhaust gas when treated with an adsorbent in an in-line exhaust pipe cannot be reasonably predicted from the results of treating the exhaust gas with the adsorbent in a looped system as disclosed in WO 94/11623 in which the exhaust gas is subjected to heat exchange before or during the

time that the exhaust gas from the adsorbent zone is contacted with the catalyst in the second catalyst zone.

Thus, the second requirement for supporting the 35 U.S.C. § 103(a) rejection is also absent.

For these reasons, EP 661,098, taken alone or in combination with WO 94/11623, cannot support a case of *prima facie* obviousness of the claims.

Referring to the 35 U.S.C. § 103(a) rejection of claims 7-22 and 26-28 over EP 602,963 ("EP '963") in view of WO 94/11623, this combination of references also fails to support a case of *prima facie* obviousness of the rejected claims for the same reasons as explained above relating to the rejection based on the combination of EP '098 and WO 94/11623. The requisite teaching, suggestion or motive to make the modification proposed by the Office is lacking. Also, the person of ordinary skill in the art could not have reasonably predicted the results of the modification proposed by the Office. In this regard, it is noted that EP '963 discloses that it is necessary to have an oxidizing gas feed means upstream of the adsorbent or adsorbent-catalyst.

For these reasons, EP 602,963, taken alone or in combination with WO 94/11623, cannot support a case of *prima facie* obviousness of the claims.

Notwithstanding the insufficiencies of the prior art to support a *prima facie* case of obviousness of the claims of the application, the data of the declaration under 37 C.F.R. § 1.132 of Akira TAKAHASHI, submitted with the response filed April 21, 2003, to the Action of January 21, 2003, provides evidence of non-obviousness sufficient to overcome any *prima facie* obviousness. The data comparing the performance of an adsorbent in an in-line system show that the exhaust system of Examples 1-9 of the present invention in which a  $\beta$ -zeolite having an SAR of 110-290 is used as an adsorbent provides unexpectedly superior results with respect to emission and purification ratio as compared to the exhaust system of Comparative Examples 1-7 in which a  $\beta$ -zeolite having an SAR of 25 to 95 is used as an adsorbent.

A notice of allowability of the claims of the application is believed to be in order and is respectfully solicited.

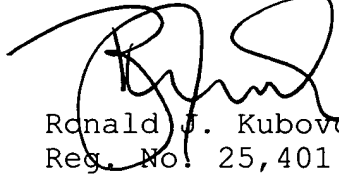
The foregoing is believed to be a complete and proper response to the Office Action dated July 1, 2003, and is believed to place this application in condition for allowance. If, however, minor issues remain that can be resolved by means of a telephone interview, the Examiner is respectfully requested to contact the undersigned attorney at the telephone number indicated below.

In the event that this paper is not considered to be timely filed, applicants hereby petition for an appropriate extension of time. The fee for any such extension may be charged to our Deposit Account No. 111833.

In the event any additional fees are required, please also charge our Deposit Account No. 111833.

Respectfully submitted,

KUBOVCIK & KUBOVCIK



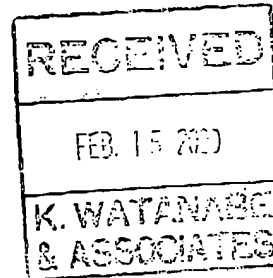
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## In-line Hydrocarbon (HC) Adsorber System for Cold Start Emissions

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NGK Insulators, Ltd.

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(SP-1260)

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# In-line Hydrocarbon (HC) Adsorber System for Cold Start Emissions

Naomi Noda, Akira Takahashi, and Hiroshige Mizuno  
NGK Insulators, Ltd.

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## ABSTRACT

In order to meet the strict automobile emission regulations in the U.S.A. and Europe, new aftertreatment technologies such as the EHC and HC Adsorber have been developed to reduce the cold start emissions.

The EHC is obviously effective in reducing emissions, but has the demerits of a large electric power demand and a complicated power control system to support it (13). A by-pass type HC adsorber system has the concerns of unreliable by-pass valves and complicated plumbing (10). A major technical challenge of the in-line type HC adsorber was the difference between the HC desorption temperature and the light-off temperature of the burn-off catalyst.

This paper describes the evaluation results of a completely passive "In-line HC Adsorber System" which can reduce the cold start emissions without the application of any type of mechanical or pneumatic control valve in the exhaust system. In summary, the NGK "In-line HC Adsorber System" has demonstrated a drastic reduction in FTP NMHC emission.

## INTRODUCTION

NGK has challenged to develop a completely passive "In-line HC Adsorber System" without using any kinds of valves.

The system consists of five components: first: light-off (LO) catalyst, second: HC adsorber which has a small center hole (BZA = Barrel-Zeolite-Adsorber), third: burn-off (BO) catalyst, fourth: main converter (MC) and fifth: secondary air pump (2nd. Air), as illustrated in figure 1.

The basic operating concept of this "In-line HC Adsorber System" is as follows:

- 1) During The Cold-Start Stage:
  - The LO catalyst is not active.
  - HC in the cold exhaust gas is adsorbed by the adsorber BZA.
- 2) In The Transition Stage:
  - Secondary air assists activation of the LO catalyst and the reaction heat generated there is transferred to the BO catalyst directly through the center hole of the adsorber BZA.
  - The BZA warms up slowly due to its large heat mass.
- 3) At Steady State Operating Conditions:
  - The BO catalyst which is already activated purifies the desorbed HC from the BZA with oxygen in the secondary air.
  - The MC catalyst purifies the residual HC.

The "In-line HC Adsorber System" has demonstrated a drastic reduction in FTP NMHC emission to the level of 0.049 g/mile when located in under-floor position on a 2.0 liter engine vehicle, even after severe engine aging equivalent to 50,000 miles.

This paper also describes the simultaneous NOx reduction of the "In-line HC Adsorber System" by utilizing secondary air injection management.

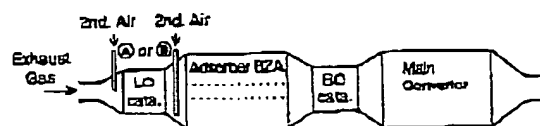


Figure 1. Illustration of the "In-line HC Adsorber System"

## EXPERIMENTAL PROCEDURE

**ACCELERATED ENGINE AGING TEST** – Although the "In-line HC Adsorber System" was tested in the under-floor position on the vehicle, it was engine aged under a more severe conditions for better reliability. The engine aging conditions are shown in table 1. This aging is equivalent to 50,000 miles in the exhaust manifold position (estimated by a Japanese automotive company). "In-line HC Adsorber System" samples were all aged as whole system illustrated in figure 1, but on the other hand small test samples of 25mm $\phi$  x 50mmL were simultaneously aged in a six-bed chamber during the accelerated thermal aging cycle.

Table 1. Accelerated Engine Aging Conditions

Equipment	: 4.5 Liter, V8 Engine
Gas Temperature	: 850°C at Inlet
Aging Cycle	: 60 Seconds Cruise Mode (A/F=14.4) and 5 Seconds Fuel Cut Mode
Duration	: 100 Hours
Aging Fuel	: Japanese Domestic Fuel (Sulfur $\leq$ 0.01 wt%)

### ZEOLITE SCREENING –

**Zeolite Samples** -- For our zeolite material evaluation, test samples A (large pore zeolite, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=110), B (medium pore zeolite, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=230) and C (large pore zeolite, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=120) were prepared by washcoating with three kinds of pre-selected zeolites onto cordierite ceramic substrates which had a 0.15 mm wall thickness and 62 cells per cm<sup>2</sup> (6 mil / 400 cpsi). The sample dimensions were 25mm $\phi$  x 50mmL (1"  $\phi$  x 2"L).

**Laboratory Adsorption Test** -- The HC adsorption capacities of the test samples were evaluated utilizing laboratory test apparatus after the engine aging. The test apparatus can mix several kinds of source gases simulating the engine cold start exhaust gas, and let the gas flow through the sample monitoring HC concentrations at Inlet and outlet position of the sample. After 300 second operation, total amount of adsorbed HC was calculated from the difference between the two HC concentrations. The detailed test conditions are shown in table 2. The adsorption test was repeated four times for one sample, with inlet gas temperature controlled at 60, 100, 140 and 180°C respectively.

Everytime HC adsorption was tested, the sample was calcined at 500°C for the sake of complete HC desorption. Toluene was used as an adsorbate because it is one of the major species in the engine

exhaust hydrocarbons.

Table 2. Laboratory Adsorption Test Conditions

Space Velocity:	40,000 per hour
Simulated Gas HC (Toluene)	5,000 ppmC
CO	2 %
CO <sub>2</sub>	16 %
H <sub>2</sub>	0.33 %
O <sub>2</sub>	0.77 %
NO	1,500 ppm
H <sub>2</sub> O	10 %
N <sub>2</sub>	Balance
(A/F=14.3)	

Inlet Gas Temperature: 60°C, 100°C, 140°C, 180°C  
Adsorption Period: 300 Seconds at each temperature

### HC ADSORBER SYSTEM DEVELOPMENT –

**System Samples for FTP Test** -- The components of the adsorber system such as the light-off catalyst (LO catalyst), barrel zeolite adsorber (BZA), burn-off catalyst (BO catalyst) and main converter (MC) were prepared by coating zeolite and/or catalyst on the cordierite ceramic substrates as described in table 3. Multiple "In-line HC Adsorber Systems" were constituted by combining one part of each major component.

Table 3. Component Parameters of the "In-line HC adsorber system"

	LO	BZA	BO	MC
<b>Dimensions:</b>				
Wall Thickness [mm]	0.10	0.15, 0.25, 0.3	0.10	0.15
Cell Density [cells/cm <sup>2</sup> ] (mil/cpsi)	62 (4/400)	62, 48.5 (5/400, 10/500, 12/500)	62 (4/400)	62 (5/400)
<b>Substrate:</b>				
Diameter [mm $\phi$ ]	53	118, 144	53	Oval
Volume [liter]	0.6	0.88-2.28	0.8	1.7
Center Hole Dia. [mm $\phi$ ]	—	25, 40	—	—
<b>Catalyst:</b>				
PM Component	Pd/Rh	Pd + Zeolite-A	Pd, Pd/Rh	Pt/Rh
PM Loading [g/liter] (g/m <sup>2</sup> )	7.07/0.12 (200/3.35) 4.24/0.49 (120/14)	Pd: 4.24 (120)	4.24 (120)	1.18/0.24 (33/8.7)

**FTP Test on a MY88 2.0 Liter Vehicle** -- After the aging at 850°C for 100 hours with a fuel cut mode, the "In-line HC Adsorber System" sample was installed in the under-floor position on a MY88 Japanese "Camry" (2.0 liter, L4 engine). FTP emission tests were conducted with Japanese domestic fuel (Sulfur  $\leq$  0.01 wt%). The test configuration is illustrated in figure 2. Secondary air was ordinarily injected into the exhaust pipe just after the O<sub>2</sub> sensor (position ④: downstream of the manifold), but was supplied from position ④ and ⑤ in the case of NO<sub>x</sub> reduction tests.

The amount of secondary air and its injection period were designed for each FTP test and are described in the test results section. For convenience of analyzing the FTP test results, Bag-1 was divided into two bags, Bag-1a and Bag-1b. Bag-1a's HC emission was a good barometer for understanding the capability of the HC adsorber system because its 0-140 second period corresponds to the critical cold start period of the engine.

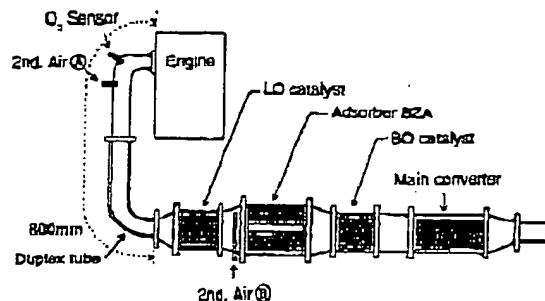


Figure 2. Illustration of FTP Test Configuration on MY88 "Camry"

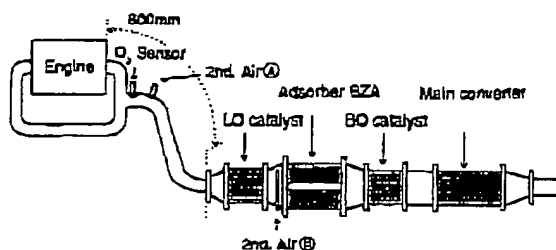


Figure 3. Illustration of FTP Test Configuration on MY95 "LeSabre"

**FTP Test on a MY95 3.8 Liter Vehicle** -- After aging at 850°C for 100 hours with a fuel cut mode, the "In-line HC Adsorber System" was installed in the under-floor position on a MY95 Buick "LeSabre" (3.8 liter, V6 engine). FTP emission tests were then carried out with Japanese domestic fuel. The FTP test configuration is illustrated in figure 3. Secondary air was injected in the same manner as in the "Camry" test case.

## TEST RESULTS

**ZEOLITE ADSORPTION TEST RESULTS** -- The toluene adsorption into large pore zeolite-A, medium pore zeolite-B and large pore zeolite-C

( $\text{SiO}_2/\text{Al}_2\text{O}_3=110, 230$  and  $120$  respectively) after the engine aging at 750°C and 850°C were determined at four inlet gas temperatures. Figure 4 compares the adsorption capabilities and thermal stability of the various zeolite materials. Zeolite-A after 750°C aging showed better adsorption capability than Zeolite-B and C. The amount of toluene adsorbed by Zeolite-A decreased to an equivalent level as Zeolite-B after 850°C aging. Zeolite-A then was selected for further system development.

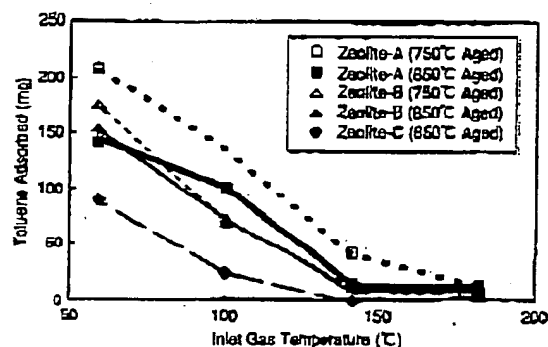


Figure 4. Toluene Adsorption Capability of Zeolite Materials

## FTP TEST RESULTS ON A MY88 2.0 LITER VEHICLE --

**Evaluation of the system concept** -- The HC adsorbed in the BZA is released around 150°C, and the BO catalyst which purifies the desorbed HC generally lights off around 300°C, after 850°C aging. In order to burn off the desorbed HC, it is necessary to compensate this temperature difference by the structural design of the system. Therefore, a 40 mmØ center hole was formed in the adsorber BZA to transfer the reaction heat from the LO catalyst to the BO catalyst for quick warm up. The LO catalyst was located upstream of the adsorber BZA so that it could light-off quickly, generate reaction heat and prevent the BZA from coking. Using the aforementioned system configuration, FTP tests were carried out to confirm the effectiveness of this system concept. Figure 5 shows the temperature profiles at the BZA outlet and BO catalyst inlet. When the temperature at the center of the BZA outlet (T1) reached 150°C, the temperature at the center of the BO catalyst inlet (T3) was 400°C, and when the peripheral portion of the BZA outlet (T2) was 150°C, the peripheral of the BO catalyst inlet (T4) was 340°C. From this data, it was concluded that the BO catalyst could light off before the HC desorption from the BZA, resolving the reversed temperature difference issue. HC emission profiles of the feed gas, the tail-pipe gas and the gas after LO catalyst were traced and are shown in figure

6. The HC emission in the feed gas could not be converted by the LO catalyst during the first 70 seconds after engine cold start. From the comparison of the HC emission profiles between after LO catalyst and tail-pipe, it was observed that only 40% of the HC emission was adsorbed in the BZA with the 40mm $\phi$  center hole, the remaining 60% flowed through the center hole without any treatment in the early stage cold start. Therefore, higher HC adsorption, in other words, more restriction of the flow-through gas was needed to further decrease HC emissions, while maintaining the resolved temperature difference.

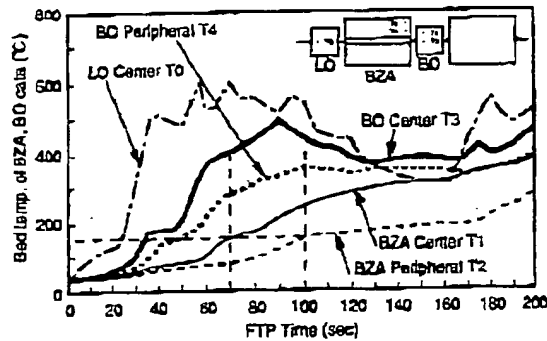


Figure 5. Temperature Profiles of BZA-outlet and BO-inlet

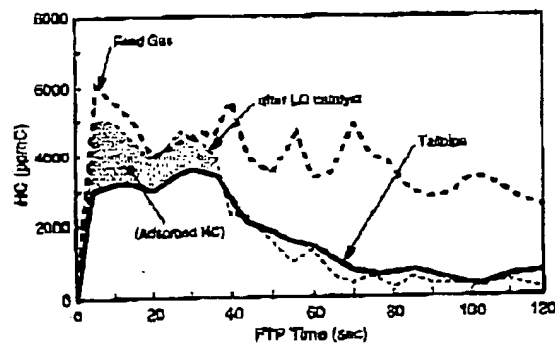


Figure 6. HC Emission Profiles at Various Points in The Exhaust System (1)

**Reduction of HC emission** — To enhance the HC adsorption in the BZA without sacrifice of the resolved temperature difference, different center hole diameters, various cell structures of substrates and different lengths of BZA were examined. The FTP test results with those sample systems are summarized in table 4.

Table 4. FTP Test Results (1)

	Baseline OEM Catalyst	In-Line HC Adsorber Systems				
		RUN-1	RUN-2	RUN-3	RUN-4	RUN-5
BZA Center Hole Dia.		40mm	35mm	25mm	25mm	25mm
Cell Structure		6/400	6/400	6/400	10/300	12/300
BZA Length		100mm	100mm	150mm	160mm	160mm
HC Emission Bag-1a (g/mile)	-	1.169g	0.950g	0.966g	0.708g	0.720g
Total HC (g/mile)	0.690	0.364	0.270	0.281	0.228	0.245
NMHC (g/mile)	0.204	0.093	0.077	0.078	0.066	0.071
CO Emission (g/mile)	-	0.075	0.058	0.081	0.049	0.054
CO Emission (g/mile)	3.874	1.324	2.067	1.862	1.522	1.503
NOx Emission (g/mile)	0.199	0.344	0.437	0.391	0.429	0.458

- \* OEM Catalyst : 1.3 liter, 37,000km accumulated in manifold position
- \*\* LO Catalyst : 0.6 liter, Pd/Rh=7.07/0.12 g/l, BO Catalyst : 0.6 liter, Pd-only=4.24 g/l
- \*\*\* Secondary Air Injection : 120 l/min., 0-200 sec.(RUN-1: 0-100 sec.), at position (A)

1) Center Hole Diameter — As the first step, the center hole diameter on the BZA was reduced from 40mm to 25mm to restrict the flow-through HC emission. The HC emission profiles of the sample systems with different center hole diameters are shown in figure 7.

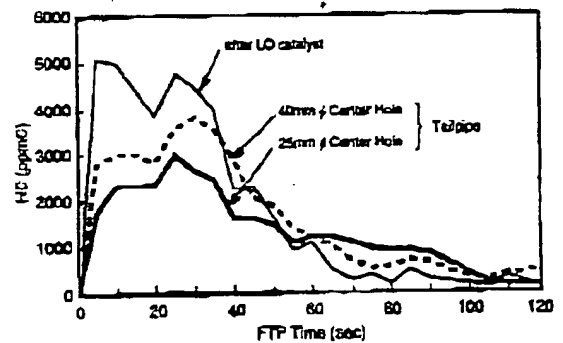


Figure 7. Effect of BZA Center Hole Diameter on Tailpipe HC

The system with smaller center hole adsorbed more HC emission than that in the case of the system with larger center hole, reducing the Bag-1a HC emission by 18% from 1.169g to 0.950g and total HC emission by 17% from 0.693 g/mile to 0.577 g/mile, these benefits were achieved although warming up of the BO catalyst peripheral (T6) was delayed 10 seconds or so (Figure 8).

Unfortunately, warm-up of the BZA outlet was faster with the smaller center hole system because more of the hot gas was diverted into the BZA. This resulted in earlier HC desorption and higher HC concentration during the 60-100 second period compared to the larger center hole system (Figure 9). Therefore, an increase in the BZA length was examined next to delay the HC desorption.

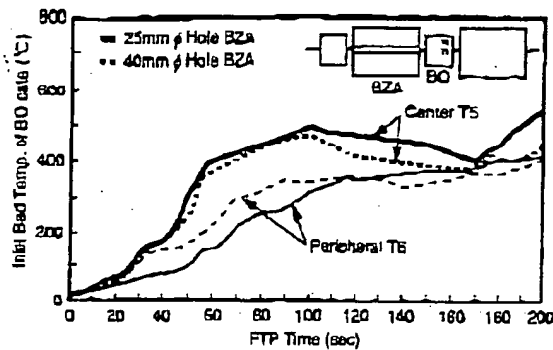


Figure 8. Inlet Bed Temperature Profiles of BO Catalyst

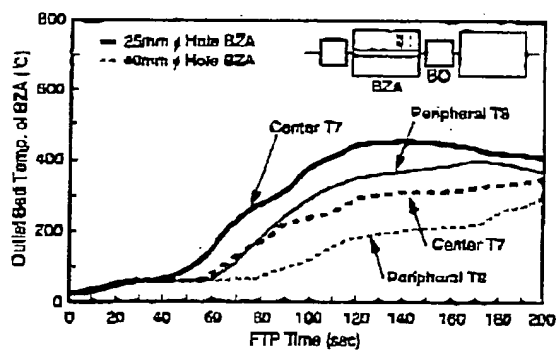


Figure 9. Outlet Bed Temperature Profiles of Adsorber BZA

- 2) Adsorber BZA Length -- The tailpipe HC emission profiles of the systems with BZAs of 100mm and 150mm length are compared in figure 10. Although HC desorption from the BZA was delayed as its length was increased, the total HC emission could not be improved. A possible reason was that the HC desorption was not delayed long enough to match with the activation time of BO catalyst. So, in addition to increasing the BZA length, the heat capacity of the BZA was increased next by changing its cell structure from 6mil/400cps to 10 or 12/300 to delay the HC desorption further.

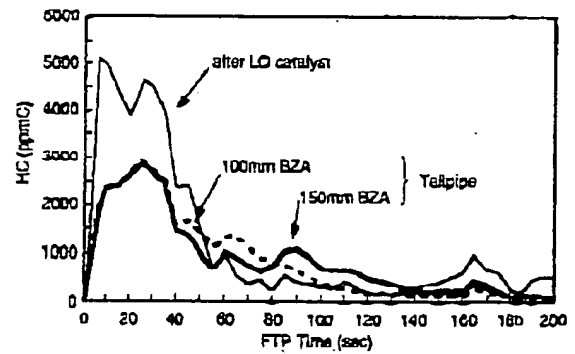


Figure 10. Effect of Adsorber BZA Length on Tailpipe HC

- 3) Cell Structure of BZA Substrate --- Figure 11 shows the tailpipe HC emission profiles of various BZA cell structures. The heat capacity increase of the BZA substrate by changing its cell structure (6/400-10 or 12 mil/300 cps) together with the increased length (100-150mm) had the desired effect of delaying the HC desorption. Furthermore, the HC amount adsorbed in the BZA was increased by using the heavier cell structures, leading to lower tailpipe HC emission.

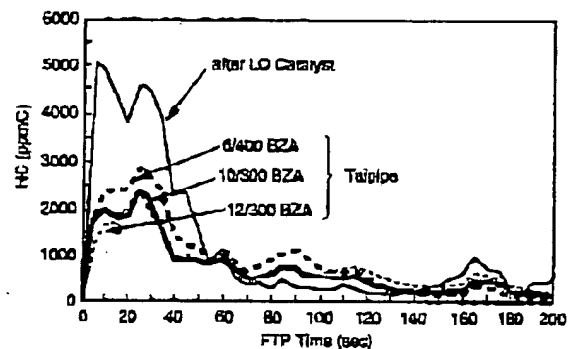


Figure 11. Effect of Cell Structure of Adsorber BZA Substrate

- 4) Interim Summary -- By using the BZA with the 25mmφ center hole, 150mm length and 10/300 cell structure, the "In-Line HC Adsorber System" could reduce FTP NMHC emission to the level of 0.049 g/mile. To examine the function of each system component, HC concentrations were traced after the LO catalyst and the adsorber BZA, as well as at the inlet-pipe (feed gas) and tail-pipe (Reference figure 12). A major portion of the untreated HC which passed through the LO catalyst during the initial 60 seconds after engine cold start was adsorbed in the BZA. Most of the desorbed HC from the BZA was converted by the BO catalyst during the 90-200 second period after

cold start. However, as shown in the table 4, the NO<sub>x</sub> emission level was extremely high compared to the ULEV standard (NO<sub>x</sub> ≤ 0.2). Therefore, for NO<sub>x</sub> reduction, secondary air injection management was studied next.

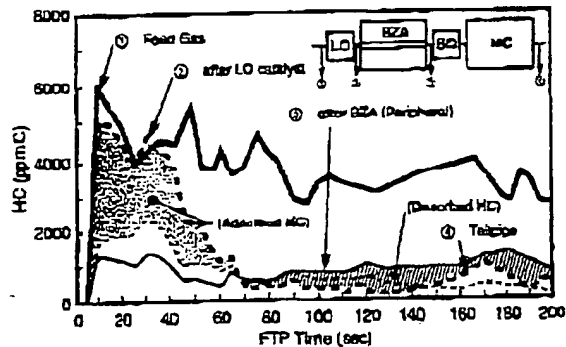


Figure 12. HC Concentration Profiles at Various Points in The Exhaust System (2)

**Reduction of NO<sub>x</sub> Emissions** – The secondary air injection management was examined to enhance NO<sub>x</sub> reduction without sacrificing the gains obtained in HC emission reduction. Figure 13 illustrates the secondary air injection procedures. In test RUN-6 and 7, air injection was switched from point ① to ② after 100 seconds from the engine cold start as illustrated in figure 13 when O<sub>2</sub> sensor started to control A/F, and was stopped after 220 seconds when a significant portion of the desorbed HC from the BZA was converted, so that the Rh on the LO catalyst could reduce the NO<sub>x</sub> being released from the lean condition. Table 5 shows the FTP test results with the various air injection management schemes. With air injection management, NO<sub>x</sub> emissions could be reduced to 0.34g/mile in RUN-6 and 0.234g/mile in RUN-7. The RUN-7 system used double LO volume of the RUN-6 system.

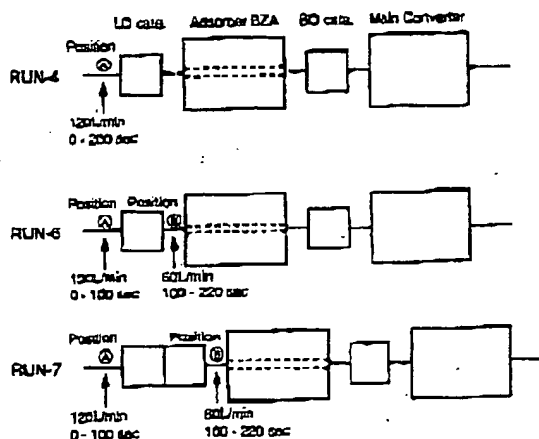


Figure 13. Secondary Air Injection Procedures (1)

Table 5. FTP Test Results (2)

	Baseline	In-Line HC Adsorber Systems		
	OEM Catalyst	RUN-6	RUN-6	RUN-7
LO Catalyst (Pd/Rh=7.07/0.12g/l)		0.6 liter	0.6 liter	0.6x2 liter
2nd. Air Injection	0	①: 120 L/min 0-200 sec	①: 120 L/min 0-100 sec ②: 80 L/min 100-220 sec	①: 120 L/min 0-100 sec ②: 80 L/min 100-220 sec
HC Emission Bag-1a (g/mile)	-	0.709g	0.873g	0.818g
Bag-1	0.69	0.228	0.272	0.271
Total HC	0.204	0.066	0.077	0.070
NMHC	-	0.049	0.057	0.056
CO Emission (g/mile)	3.874	1.522	0.985	0.838
NO <sub>x</sub> Emission (g/mile)	0.199	0.429	0.340	0.234

- \* OEM Catalyst : 1.3 liter, 37,000km accumulated in manifold position
- Adsorber BZA : 118mmØ/25mmØ × 150mmL, 10/300 Cell, Pd:4.24g/l+Zeolite-A coated
- BO Catalyst : 0.8 liter, Pd-only=4.24g/l

**FTP TEST RESULTS ON A MY95 3.8 LITER VEHICLE** – The same "In-line Adsorber System" as used in RUN-7 on the Toyota "Camry" was tested on a Buick "LeSabre", which has a larger engine displacement (3.8 liter vs. 2.0 liter). Figure 14 illustrates the air injection procedure for this test vehicle. In the case of the "LeSabre", air injection was switched from point ① to ② after 70 seconds from engine cold start because the A/F control on the "LeSabre" had started a little earlier than on the "Camry". This was due to the Buick's HEGO sensor. The FTP test results are summarized in table 6. Although the "LeSabre" emits more feed gas HC and, what is worse, warms up the adsorber BZA faster than the "Camry" due to its large engine displacement, the NMHC emission could be reduced to 0.052g/mile, almost the same low emission level as obtained on the "Camry", with good NO<sub>x</sub> of 0.162g/mile in RUN-8. Moreover, when the longer length BZA was applied to the system to address the higher V6 engine exhaust flow, NMHC emission was further reduced to 0.049g/mile with 0.200g/mile of NO<sub>x</sub> emission as shown in the RUN-9 data. In the same manner as the case of "Camry", HC concentrations in the RUN-9 were traced after the LO catalyst (for the initial 60 seconds) and the adsorber BZA (after 60 second) as well as at the inletpipe and tailpipe (Reference figure 15).

It was confirmed again that each system component functioned well. A major portion of untreated HC was adsorbed in the BZA during the initial 35 seconds, and most of the desorbed HC from the BZA was converted by the BO catalyst during the 190-300 second period after cold start.

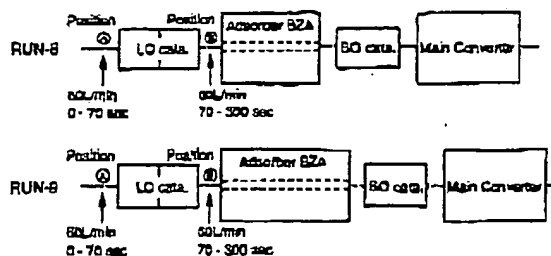


Figure 14. Secondary Air Injection Procedures (2)

Table 6: FTP Test Results (3)

		Baseline		In-Line HC Adsorber Systems	
		Feed Gas	OEM Catalyst	RUN-8	RUN-9
System Components	LO Catalyst			0.6x2 liter Pd/Rh=4.24/0.48g/l	0.6x2 liter Pd/Rh=4.24/0.48g/l
	Adsorber BZA			110mmφx150mmL 10/300 Cell 25mmφhole	110mmφx150mmL 10/300 Cell 25mmφhole
	BO Catalyst	0	0	0.6 liter Pd-only=4.24g/l	0.6 liter Pd-only=4.24g/l
2nd. Air Injection				①: 60 l/min. 0-70 sec. ②: 60 l/min. 70-300 sec.	①: 60 l/min. 0-70 sec. ②: 60 l/min. 70-300 sec.
FTP Emission (g/mile)	Total HC Reduction	1.862	0.112	0.068	0.065
	NMHC	1.800	0.098	0.052	0.048
	CO	11.538	1.083	0.768	0.638
	NOx	2.166	0.086	0.162	0.200

\* OEM Catalyst : 2.5 liter (two bricks), 13,000km (8,000 Miles) accumulated in under-floor position

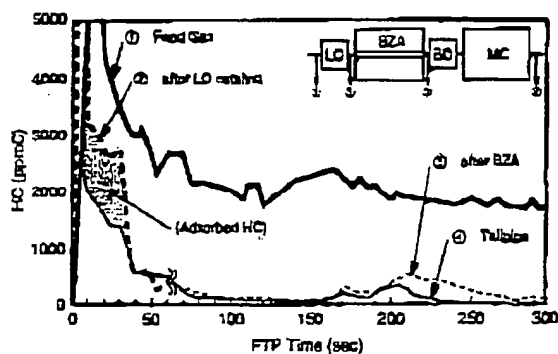


Figure 15. HC Concentration Profiles at Various Points in The Exhaust System (3)

## SUMMARY AND CONCLUSIONS

- 1) The "In-line HC Adsorber System" which consists of LO Catalyst + Adsorber BZA with a center hole + BO Catalyst + Main Converter and secondary air injection management showed the capability of resolving the reversed temperature difference between the HC desorption temperature from BZA and the light-off temperature of BO catalyst without the use of flow control valves or air curtains.
- 2) This completely passive "In-Line HC Adsorber System" demonstrated a drastic reduction in FTP NMHC emission to the level of 0.048g/mile when located in under-floor position on a 2.0 liter Japanese car and a 3.8 liter American car with Japanese domestic fuel even after severe engine aging equivalent to 50,000 miles in the exhaust manifold. In the case of the 3.8 liter American car, 0.048g/mile NMHC emission corresponded to 97.2% reduction from the feed gas level.
- 3) Through an air injection management system which could benefit the Rh catalyst on the LO converter, NOx was reduced to the ULEV level.
- 4) Duration of the after-treatment by adsorber system should be shortened as much as possible. With this "In-Line HC Adsorber System", it was within 300 seconds on a 3.8 liter American car.
- 5) The "In-Line HC Adsorber System" described here met LEV regulation even with Japanese domestic fuel without oxygenate, and is expected to be a potential technology for clearing ULEV standard when it is operated with a clean fuel such as Phase-2 gasoline.

We could have the good initial results as summarized above, but have many more questions to address. What further studies does NGK have planned :

- FTP test on a latest cleaner car with the phase-2 gasoline to confirm the capability of meeting the ULEV standard.
- 100,000 miles durability test.
- Backpressure penalty check.
- Adsorption capacity study for multi cold-start capability.
- OBD-2 countermeasure, and so on.



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## **In-line Hydrocarbon Adsorber for Cold Start Emissions - Part II**

**Naomi Noda, Akira Takahashi, Yukinari Shibagaki and Hiroshi Mizuno**  
NGK Insulators, Ltd.

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## In-line Hydrocarbon Adsorber for Cold Start Emissions - Part II

Naomi Noda, Akira Takahashi,  
Yukinari Shibagaki and Hiroshige Mizuno  
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### ABSTRACT

The in-line hydrocarbon (HC) adsorber is a passive aftertreatment technology to address cold-start hydrocarbons in automotive engine exhaust gas. A major technical challenge of the in-line HC adsorber is the difference between the HC release temperature of the adsorber and the light-off temperature of the burn-off (BO) Catalyst. We call this phenomenon the "reversed-temperature difference".

To reduce the reversed temperature difference, NGK has proposed a new "In-line HC Adsorber System" which consists of light-off (LO) Catalyst, Barrel Zeolite Adsorber (BZA) with a hole through the center, BO Catalyst and secondary air injection management (SAE 970266).

This, our latest paper, describes the evaluation of various adsorbents and the effect of the center hole on the Adsorber BZA.

The adsorber system, which had the Adsorber BZA with a 25mm  $\phi$  center hole and adsorbent coated, confirmed 30% lower FTP NMHC emission versus a system with no center hole or adsorbent coating. These two systems had been RAT-A engine aged to an equivalent to 50,000 miles, and tested in the under-floor position on a vehicle equipped with a 3.8 liter engine. Further, adsorption and desorption performance of the adsorber BZAs and heat up rates of the BO Catalysts with different BZA center hole diameters are also discussed.

This In-line HC Adsorber System could be one of the potential technologies to meet LEV/ULEV and Stage-3/Stage-4 regulations, without suffering from thermal deterioration of the close-coupled catalyst in the manifold area.

### INTRODUCTION

NGK has proposed the following "In-line HC Adsorber System" in our previous paper (SAE 970266) in order to reduce the reversed temperature difference between the HC desorption temperature (around 150°C) and the light-off temperature of burn-off catalyst (above 300°C). This is the most critical issue for in-line type adsorber systems.

The In-line Adsorber System consists of four components in series: first: light-off (LO) catalyst; second: HC adsorber which has a small center hole (BZA = Barrel Zeolite-Adsorber); third: burn-off (BO) catalyst; fourth: secondary air pump (2nd. Air), as illustrated in Figure 1.

The basic operating concept of the In-line HC Adsorber System is as follows:

#### (1) During The Cold Start Stage:

- The LO catalyst is not active.
- HC in the cold exhaust gas is adsorbed by the adsorber BZA.

#### (2) In The Transition Stage:

- Secondary air assists activation of the LO catalyst and the reaction heat generated there is transferred to the BO catalyst directly through the center hole of the adsorber BZA.
- The BZA warms up slowly due to its large heat mass.

#### (3) At Steady State Operating Conditions:

- The BO catalyst which is already activated purifies the desorbed HC from the BZA with oxygen in the secondary air.

Our previous paper, #970266, involved the evaluation of A) three zeolite materials, B) various configurations of the BZA including different outer diameters, lengths, substrate wall thickness & cell densities, center hole diameters, and C) secondary air strategies.

This paper is an update of our detailed study on the effects of the adsorbent and center hole on the adsorber BZA in the NGK In-line HC Adsorber System. Furthermore, the optimum center hole diameter for the new test vehicle, a MY97 Buick "LeSabre" (3.8 liter, V6 engine), is also discussed from the viewpoint of HC adsorption efficiency and desorbed HC conversion efficiency.

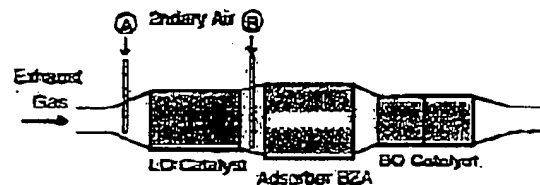


Figure 1. Illustration of the "In-line HC Adsorber System"

## EXPERIMENTAL PROCEDURE

## LABORATORY ZEOLITE AGING TEST

A large pore size zeolite, Zeolite-A, as described in our previous paper SAE 970266, showed high toluene adsorption capability. In order to evaluate the influence of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on the thermal stability of Zeolite-A, two different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio zeolites, Zeolite-A1 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=70$ ) and Zeolite-A2 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=270$ ), were examined. The zeolite powder was aged at an elevated temperature for 4 hours in the atmosphere of 10vol%  $\text{H}_2\text{O}$ , 8vol%  $\text{CO}_2$ , 1vol%  $\text{O}_2$ , and 81vol%  $\text{N}_2$ . The specific surface area of the powder was measured by the BET  $\text{N}_2$  adsorption method ( $P/P_0=0.3$ ).

## SYSTEM SAMPLES

The components of the adsorber system, such as the light-off catalyst (LO catalyst), barrel zeolite adsorber (BZA) and burn-off catalyst (BO catalyst), were prepared by coating zeolite and/or catalyst on the cordierite ceramic substrates as described in Table 1. Multiple In-line HC Adsorber Systems were constituted by holding the LO & BO components fixed and changing adsorber BZA parameters. A '97 California TLEV OEM catalytic converter (California emission), which consisted of three bricks (first: Pd only, 0.8 liter, second: Pt/Rh, 0.7 liter, third: Pt/Rh, 1.3 liter), was also used as the baseline.

Table 1. Component Parameters of the In-line HC Adsorber System

	Major Components		
	LO	BZA	BO
Dimensions:			
Wall Thickness [mm]	0.1	0.3	0.1
Cell Density [cells/cm <sup>2</sup> ] (mil/cpsi)	62 (4/400)	46.5 (12/300)	62 (4/400)
Substrate:			
Diameter [mm $\phi$ ] (Inch $\phi$ )	106 (4.16)	118 (4.66)	93 (3.66)
Volume [liter]	1.2	1.5	0.6X2pcs
Center Hole Dia. [mm $\phi$ ]	-	0, 25, 32, 40	-
Coating:			
Zeolite	-	Zeolite-A2    None-Zeo.	-
Zeolite Loading [g/liter]	-	120            0	-
		+                +	
Catalyst	Pd/Rh	Pd              Pd	Pd + Pt/Rh
PM Loading [g/liter] (g/h <sup>3</sup> )	7.07/0.25 (200/7)	4.24 (120)	4.24 (120)
			7.07   1.18/0.24 (200)   (33.3/6.7)

## ACCELERATED ENGINE AGING TEST

In-line HC Adsorber Systems and the OEM converter were dyno aged using the RAT-A cycle (rapid aging test) which was described in SAE paper 940742. For the test vehicle with a 3.8 liter-V6 engine, 30 hours of aging was

regarded as equivalent to 50,000 vehicle miles. The details of the RAT-A cycle are shown in Table 2. During the aging, the maximum inlet bed temperature of the LO catalyst was around 850°C.

Table 2. RAT-A Aging Cycle Specifications

Segment	Engine Operation	Duration (seconds)
1*	Stoichiometry	40
2	Fuel-Rich	6
3	Fuel-Rich with Air Injection	10
4	Stoichiometry with Air Injection	4

\* Inlet gas temperature should be set at  $800 \pm 10^\circ\text{C}$

**FTP TEST**--After 50,000 mile equivalent dyno aging, the In-line HC Adsorber System was installed in the under-floor position on a MY97 Buick LeSabre (3.8 liter, V6 engine). FTP emission tests were then carried out with Phase II fuel. The FTP test configuration is illustrated in Figure 2.

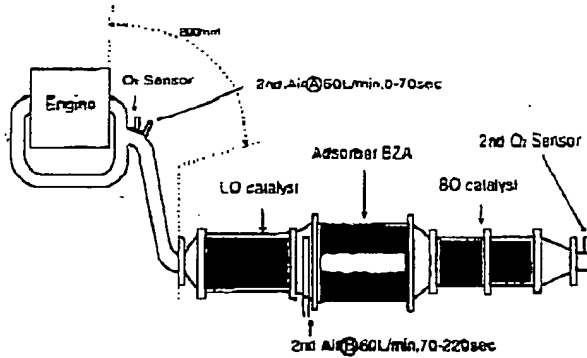


Figure 2. Illustration of FTP Test Configuration on MY97 Buick "LeSabre"

Eight different In-line HC Adsorber Systems were tested to investigate the following items:

- 1) Adsorbent evaluation (comparison between with and without zeolite) and center hole evaluation (comparison between with and without center hole)
- 2) Optimum Adsorber BZA center hole diameter on Adsorber BZA for the test vehicle
- 3) Advantage over the MY97 Buick LeSabre production exhaust system (California TLEV OEM catalytic converter)

In all FTP tests, secondary air was injected for the initial 220 seconds of cold start at a rate of 60L/min. However, the air injection position was switched from (A) to (B) as soon as the LO catalyst was activated. The secondary air management allowed the Rh coated on the LO catalyst to reduce NOx being released from the lean condition.

Table 3. Secondary Air Management

Time	Position	Purpose
0-70 sec	(A): Downstream of the manifold	To assist LO catalyst activation
70-220 sec	(B): Between LO catalyst and Adsorber BZA	To supply Oxygen for burning off the desorbed HC

## TEST RESULTS

### ZEOLITE AGING TEST RESULTS

Figure 3 compares the specific surface areas of Zeolite-A1 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=70$ ) and Zeolite-A2 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=270$ ) after aging at each temperature. Specific surface areas of both Zeolite-A1 and Zeolite-A2 decreased with the aging temperature increase. Decrease of specific surface area is caused by the degradation of zeolite pore structure, which leads to the decrease of HC adsorption capacity. As a result, the Zeolite-A2 with higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio provided greater thermal stability. Therefore, it was selected for further system development.

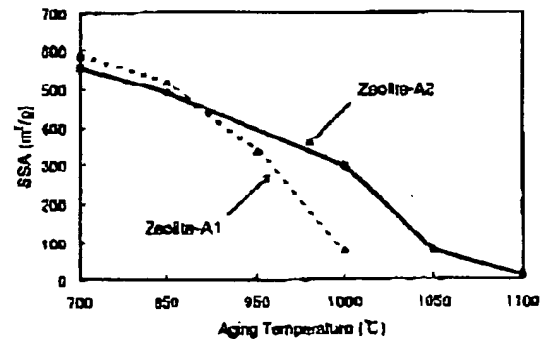


Figure 3. Thermal Stability Improvement of Zeolite-A

### FTP TEST RESULTS

FTP test results including those of the blank system (LO catalyst + BO catalyst only) and the OEM converter are listed in Table 4.

Table 4. FTP Emission Results

Center Hole on Adsorber BZA				No Hole	25mm $\phi$	32mm $\phi$	40mm $\phi$	Blank *	(OEM conv)**
(g/mile) FTP Emission									
Adsorber Component	Zeolite-A2 + Pd cata (w/ zeo)	HC	Bag 1	1.204	0.885	1.112	1.142		
			THC	0.078	0.061	0.076	0.079		
			NMHC	0.065	0.047	0.061	0.063		
		NOx		0.19	0.28	0.19	0.24		
		CO		1.02	0.88	0.96	0.83		
	Pd cata only (w/o zeo)	HC	Bag 1	1.230	1.201	1.429	1.347	1.534	1.436
			THC	0.082	0.077	0.082	0.081	0.104	0.093
			NMHC	0.067	0.063	0.076	0.075	0.085	0.079
		NOx		0.22	0.27	0.21	0.23	0.26	0.31
		CO		0.99	0.87	1.16	0.85	1.26	1.05

\* LO catalyst + (vacant can) + BO catalyst  
Secondary air was supplied in the same manner as other tests.

\*\* OEM converter only  
Secondary air was injected only from position ① throughout initial 220 seconds.

#### 1) Adsorbent effect and center hole effect

Bag 1 represents the HC reduction performance of the In-line HC Adsorber System during the cold start phase.

All the adsorber systems with the zeolite-coated BZA showed lower HC emissions than systems with no zeolite coating on the BZA. This was true for all different center hole diameters. Therefore, the zeolite "adsorbent effect" in reducing cold start HC emission was confirmed. This means that the Zeolite-A2 could adsorb unburned HC even after the 50,000 mile accelerated engine aging. Also, a portion of the desorbed HC from the Zeolite-A2 could be purified by the BO catalyst.

For zeolite coated adsorber systems, all systems with the hole in the BZA demonstrated lower Bag 1 emissions than that of the system with a "hole-less" BZA. Therefore, this proved the hole in the BZA reduced cold start HC emissions.

On the other hand, in the case of no-zeolite adsorber systems, though they were no longer adsorber systems, the center holes offered no particular advantage in reducing cold start HC emission. This means that the benefits of the BZA "center hole" is peculiar to the zeolite-coated adsorber system.

Furthermore, in the case of "no-hole" adsorber systems, there was very little HC emission difference between the systems with and without zeolite coatings. These results indicate the BZA with zeolite released HC before the following catalyst became active.

As a result, our conclusion was that both adsorbent and center hole on the BZA could work synergistically to reduce the cold start HC emission effectively.

#### 2) Optimum center hole diameter

In general, the performance of HC adsorber system depends on the following two factors:

- 2-1) HC adsorption efficiency
- 2-2) Conversion efficiency of the desorbed HC

Those two factors are greatly influenced by the BZA hole diameter in the case of the NGK In-line HC Adsorber System.

Naturally, a larger center hole in the adsorber BZA leads to not only less "HC adsorption", a disadvantage, but also higher "desorbed HC conversion", an advantage. The advantage results from higher exhaust gas & heat flow through the center hole and faster warm-up of the BO catalyst. On the contrary, a smaller center hole in the Adsorber BZA causes greater HC adsorption as well as lower desorbed HC conversion. There is a "trade-off" between "HC adsorption efficiency" and "desorbed HC conversion efficiency".

The FTP test results in Table 4 of "with-hole" BZAs revealed that the adsorber system with a 25mm  $\phi$  hole gave the best Bag 1 HC emissions.

To understand this trade-off, we have studied the reason why Bag 1 HC emissions decrease in the order of decreasing hole sizes in BZA: no hole  $\rightarrow$  40mm  $\phi$   $\rightarrow$  32mm  $\phi$   $\rightarrow$  25mm  $\phi$  on BZA.

#### 2-1) HC adsorption efficiency:

Figures 4A-4D show the tailpipe HC concentration profiles of both zeolite coated and no-zeolite adsorber systems for each center hole diameter on BZA.

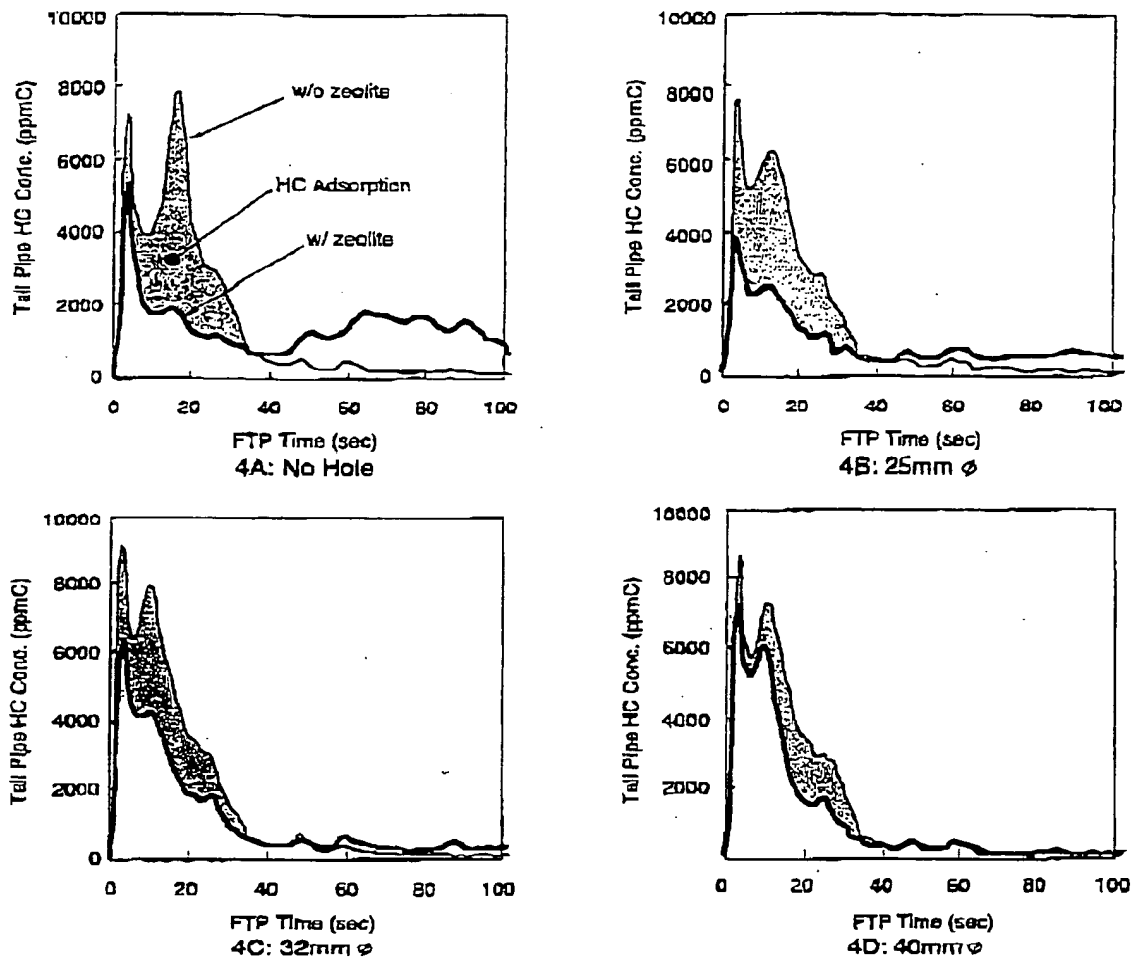


Figure 4. Tail Pipe HC Concentration Profiles in the Systems with Various Center Hole Diameters

The HC concentration difference between the with and without zeolite systems in the early stages of cold start defines the HC adsorption. Therefore, we defined the HC emission difference between with and without zeolite systems for the initial 45 seconds as "HC adsorption (g/0-45sec)".

HC adsorptions for the systems with each center hole diameter are summarized in Table 5. The trend that the HC adsorption was decreased as the hole in BZA grew was reasonable, and the 40mm  $\phi$  center hole on BZA was found to lose HC adsorption considerably.

Table 5. "HC Adsorption"

BZA Center Hole Diameter	No Hole	25mm $\phi$	32mm $\phi$	40mm $\phi$
HC Adsorption (g/0-45sec)	0.50	0.43	0.44	0.32

## 2-2) Conversion efficiency of desorbed HC:

First of all, we checked whether the larger center hole in the BZA could lead to the faster heat up of the BO catalyst.

Figures 5A - 5D show temperature profiles monitored at both adsorber outlet (center :  $T_1$ , periphery :  $T_2$ ) and BO catalyst inlet (center :  $T_3$ , periphery :  $T_4$ ) for each hole diameter. It was confirmed that heating up of the BO catalyst (particularly the periphery) was promoted as the center hole diameter on the BZA was increased.

The large center hole in the BZA was found to have a sub-effect of delaying the HC desorption from the BZA. This was because the larger hole in the BZA allowed more exhaust gas flow through the center hole, resulting in less gas flow in the peripheral portion of the BZA, reducing its warm-up rate & delaying "desorption". The slower HC desorption is preferable for the BO catalyst to have more time to warm up.

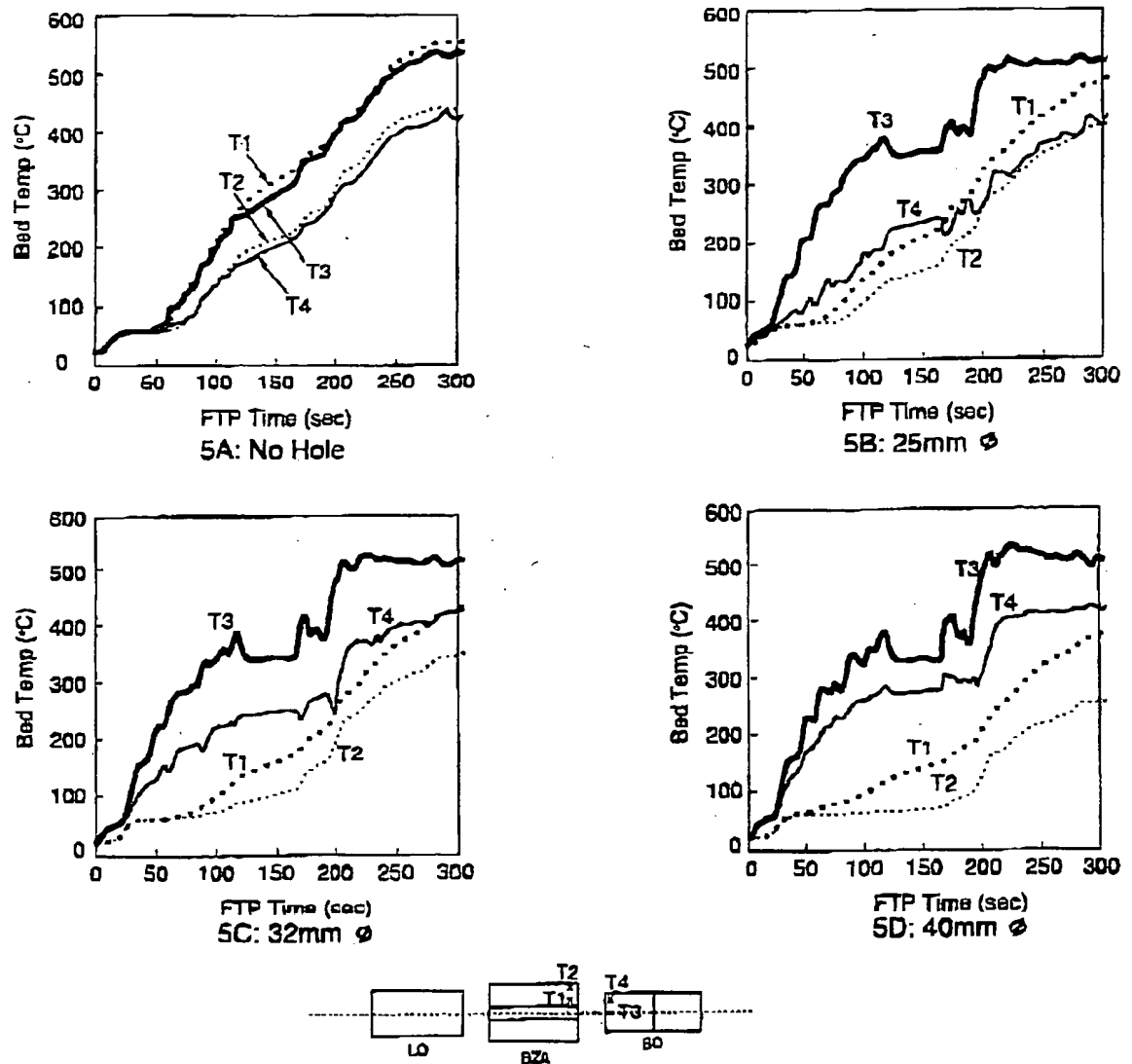


Figure 5. Temperature Profiles at Adsorber Outlet and BO Catalyst Inlet

The time when the outlet of the BZA reached 150°C, which is ordinarily regarded as HC desorption temperature, and the corresponding inlet bed temperature of the BO catalyst were summarized in

Table 6. In summary, the larger center hole in the BZA was advantageous over the smaller one for quicker heat up of the BO catalyst, especially at the peripheral portion before the HC desorption from the BZA.

Table 6. Inlet bed temperatures of the BO Catalyst when outlet bed temperature of the Adsorber BZA reached 150°C

BZA Center Hole	No Hole		25mm $\phi$		32mm $\phi$		40mm $\phi$	
	Center	Periphery	Center	Periphery	Center	Periphery	Center	Periphery
Times needed for outlet bed of the Adsorber BZA to reach up to 150°C (second)	103	83	108	145	138	181	165	206
Inlet bed temperatures of the BO Catalyst at the above times (°C)	219	85	359	234	341	277	342	338



Next, desorbed HC conversion efficiency was examined.

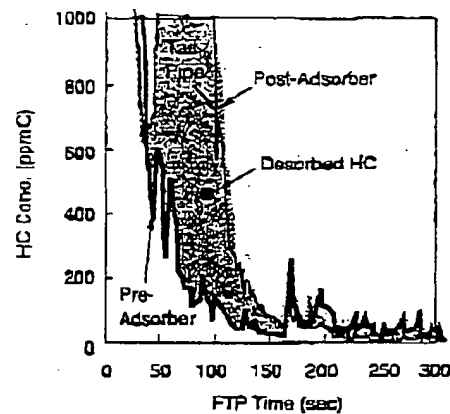
Figures 6A - 6D show HC concentration profiles monitored at the following three positions: pre-Adsorber BZA, post-Adsorber BZA and tailpipe.

In any cases, unburned HCs in the feed gas were adsorbed into the adsorber for the initial 40-50 seconds of cold start.

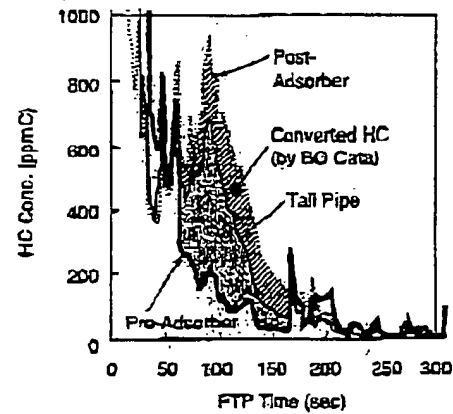
When the HC concentration monitored at the post-adsorber position gets higher than that at the pre-adsorber position, the difference between them is "desorbed HC". It was confirmed that the larger center hole tended to

increase delay of the HC desorption. It was also confirmed that a substantial amount of the adsorbed HC was desorbed when the outlet bed of the adsorber reached 150°C.

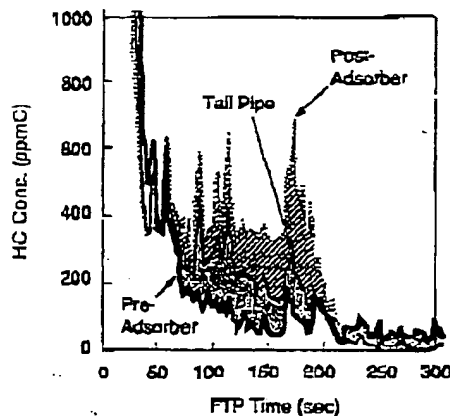
On the other hand, the HC concentration difference between the post-adsorber and tailpipe indicates the converted HC by the BO catalyst. Again, it was confirmed that the larger center hole on the BZA, which allowed the BO catalyst to heat up more rapidly, led to a higher HC conversion.



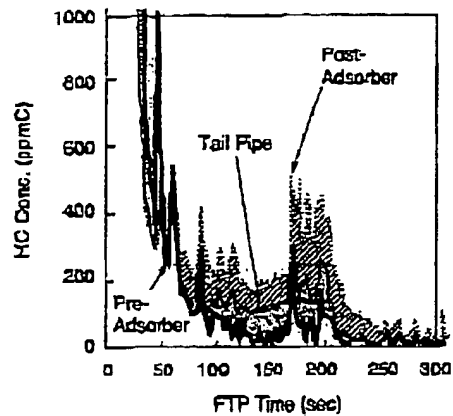
6A: No Hole



6B: 25mm  $\phi$



6C: 32mm  $\phi$



6D: 40mm  $\phi$

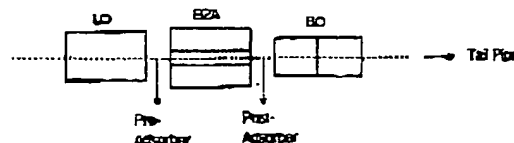


Figure 6. HC Concentration Profiles at Each Position

Table 7 proves the above-mentioned trend with modal mass data. Here, the desorbed HC conversion efficiency was given by dividing the amount of HC converted by the BO catalyst by the amount of HC desorbed from the BZA. This trend is reasonable when referring to the temperature and HC concentration profiles.

Table 7 also clarified that in the case of the no-hole adsorber system, very little of the desorbed HC could be converted by the BO catalyst. And also, there was no additional improvement in the desorbed HC conversion efficiency of the 40mm  $\phi$  hole adsorber system compared to that of the 32mm  $\phi$  hole adsorber system.

Table 7. Desorbed HC Conversion Efficiency by BO Catalyst

BZA Center Hole	No Hole	25mm $\phi$	32mm $\phi$	40mm $\phi$
Desorbed HC Conversion Efficiency (%)	5.7	40.3	59.7	59.9

As the result of the trade-off relationship between the HC adsorption efficiency and the desorbed HC conversion efficiency in regard to the BZA center hole diameter, it was concluded that the center hole diameter of 25mm  $\phi$  was well-balanced to provide the lowest HC emission among the tested sample systems on this vehicle.

However, 25mm  $\phi$  will not always be the best hole diameter for every engine platform, because both HC adsorption efficiency and desorbed HC conversion efficiency greatly depend on the total flow gas volume and its temperature and on the gas flow ratio between the center hole and the peripheral adsorber portion.

Therefore, it is essential to optimize the adsorber system including the center hole diameter for each different engine platform for the lowest emissions.

### 3) Advantage over the MY97 Buick LeSabre exhaust system.

HC emission of the MY97 Buick LeSabre equipped with a California TLEV OEM catalytic converter which was engine aged to 50,000 miles equivalent was compared with the In-line HC Adsorber Systems in Table 4.

Secondary air was also supplied to the OEM converter during the FTP tests under the same condition as in the cases of the adsorber systems. However, in all cases with the In-line HC Adsorber Systems, even with the no-hole adsorber system, the HC emissions were lower than that in the case with the OEM converter. Particularly, the In-line HC Adsorber System with the 25mm  $\phi$  BZA demonstrated 40% lower NMHC emission compared with the emission with the OEM catalytic converter.

## SUMMARY

- NGK In-line HC Adsorber System with a center hole on the zeolite coated BZA provided lower HC emission than that of the system A) with a center hole on the BZA and no-zeolite coating, and B) a system without a center hole in the zeolite coated BZA, when installed in under-floor position on MY97 Buick LeSabre (3.8 liter, V6 engine). The benefits of the zeolite coating and center hole on the Adsorber BZA were confirmed.

- In terms of the center hole size on the adsorber BZA, a 25mm  $\phi$ -hole provided well-balanced performance in reducing of HC emissions considering the trade-off relationship between HC adsorption efficiency and desorbed HC conversion efficiency on a MY97 Buick LeSabre. The "optimum", 50,000 mile aged In-line HC Adsorber System had FTP by NMHC emissions of 0.047g/mile, but exceeds ULEV which are our development goals.
- NGK In-line HC Adsorber System with 25mm  $\phi$  center hole on the adsorber BZA reduced NMHC emissions 40% below the baseline, California TLEV OEM Converter for the MY97 Buick LeSabre.

## FUTURE STUDIES

We experienced relatively high emission levels in this test round at SwRI, due to an engine control system problem on the test vehicle. However, we believe that the data from these tests can be used to rank the performance of the sample adsorbers.

Therefore, our next step will be to check the real absolute FTP emission level of the optimized In-line HC Adsorber System for the MY97 LeSabre, when the engine control system is corrected.

The future studies we will conduct are:

- NOx reduction by limiting the secondary air injection
- Adsorption capacity study for multi cold-start capability
- Backpressure penalty check
- Isostatic strength check of the center holed ceramic honeycomb
- OBD-2 countermeasure

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## **In-line Hydro Carbon Adsorber**

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NGK-Locke Inc.

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1999-01-1230

# In-line Hydrocarbon Adsorber

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## ABSTRACT

The in-line hydrocarbon(HC) adsorber is one type of passive after-treatment technology which can reduce the cold start hydrocarbon from automobile engine exhaust gas. However, major technical issues to be resolved for practical use of this system are 1)the temperature difference between HC desorption from the adsorbent and activation of the catalyst to burn-off the desorbed HCs and 2)the ability to adsorb a wide range of HC molecule sizes in the cold exhaust gas.

Recent zeolite development has resulted in an unique adsorbent capable of adsorbing small HC molecules as well as large to some degree, even under aqueous conditions. This adsorbent also features a relatively high HC desorption temperature. As a result, an in-line HC adsorber system has been developed, which can trap more unburned HCs during the engine cold start phase and burn-off the desorbed HCs more efficiently in the desorption phase by using this unique adsorbent. This HC adsorber system demonstrated a drastic reduction in FTP NMHC emission.

This paper describes our evaluation results of the improved HC adsorber including a discussion on the thermal durability of the adsorbent.

This in-line HC adsorber system is one of the viable tools to address future tighter regulations as a "stand-alone" system or as a component within other after-treatment systems to increase their effectiveness.

## 1) INTRODUCTION

In our previous SAE papers 970266 and 980423, NGK Insulators, Ltd. has proposed the In-line Hydrocarbon(HC) Adsorber System to address cold start emissions, which included a HC adsorber component with a center hole, followed by a burn-off catalyst (Figure 1). The center hole provided a direct flow(heat) path for the exhaust gas to the burn-off catalyst. This design feature compensated for the temperature difference between HC desorption from the adsorbent and activation of the burn-off catalyst. However, this design also required a trade-off between HC adsorption efficiency and conversion efficiency of the desorbed HCs, because the center hole sacrificed HC adsorption efficiency.

Therefore, in our latest phase of development, we have addressed the challenge of eliminating the center hole of the adsorber component by improving the adsorbent material to retain the HC molecules until the catalyst activation temperature is obtained. A key feature of this generation HC adsorber system is the desorbed HCs from the improved adsorbent are burned-off by the catalyst component coexisting with it on the adsorber, so that high adsorption efficiency and high desorbed HC conversion efficiency were achieved simultaneously.

Then, taking advantage of the excellent adsorption capability to trap fine HC molecules as well as large proven with this unique adsorbent, provided a means to further improve HC adsorption efficiency, another technical challenge for the HC adsorber system.

Furthermore, while evaluating the advantageous characteristics of this new adsorbent, a detailed study on its thermal stability was conducted. Thermal stability was the sole concern we had for the practical use of this adsorbent.

For the evaluation of the forementioned objectives, laboratory tests using a model gas and on-vehicle FTP tests were adopted. The experimental procedure and test results of the laboratory and vehicle test are discussed in section II and III.

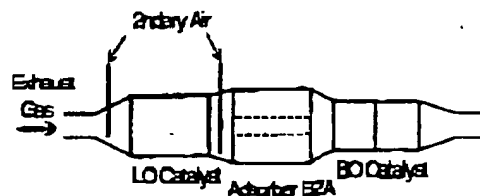


Figure 1. Illustration of the "In-line HC Adsorber System"

## II) EXPERIMENTAL PROCEDURE

### II-1) LABORATORY ADSORPTION TEST

#### i) Sample Preparation:

Zeolite-AX was obtained modifying the H-type Zeolite-A (large pore zeolite,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 150$ ) with an additive X. Test samples for measuring HC adsorption were prepared by

washcoating the Zeolite-AX onto cordierite honeycomb substrates (6mil/400cpsi, 25mm $\phi$  = 50mm<sup>2</sup>), to a fixed loading of 160g/liter each.

### ii) Accelerated Engine Aging:

The prepared laboratory test samples were mounted on the six-bed chamber (Figure 2) and exposed to engine aging under the accelerated engine aging conditions shown in Table 1. The aging is equivalent to 50,000 vehicle miles in the under-floor position when carried out at the inlet gas temperature of 750°C.

\*Estimated by a Japanese automotive company.

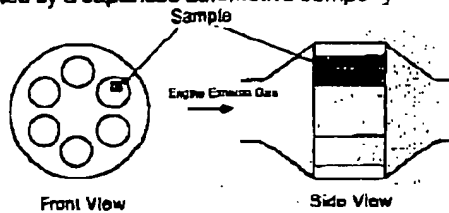


Figure 2. Six-bed Chamber

Table 1. Accelerated Engine Aging Conditions

Equipment	: 4.5liter, V8 Engine
Gas Temperature	: 800, 750°C at Inlet
Aging Cycle	: 60 Seconds Cruise Mode and 5 Seconds Fuel Cut Mode
Duration	: 100 Hours
Aging Fuel	: Japanese Domestic Fuel (Sulfur ... 0.01wt%)

### iii) Adsorption Test:

After engine aging, the HC adsorption capacities of the test samples were evaluated in a laboratory test apparatus with simulated automotive gas mixture. The gas mixture flowing through the sample is monitored for HC concentrations at the inlet and outlet of the sample. After 300 seconds of operation, the total amount of adsorbed

HC was calculated from the difference between the inlet and outlet HC concentrations.

Table 2. Laboratory Adsorption Test Conditions

Space Velocity	: 40,000/hour
Simulated Gas Mixture	: (A/E-14.3)
HC	: 0.000000C
(Toluene or Propylene)	
CO	: 2%
CO <sub>2</sub>	: 10%
H <sub>2</sub>	: 0.33%
CH <sub>4</sub>	: 0.77%
NO	: 1.500ppm
H <sub>2</sub> O	: 10%
N <sub>2</sub>	: Balance
Inlet Gas Temperature	: 60, 100, 140, 180, 260, 340°C
Adsorption Period	: 300 Seconds
at each temperature	

The detailed test conditions are shown in Table 2.

The adsorption test was repeated six times for each sample, with inlet gas temperature controlled at 60°C, 100°C, 140°C, 180°C, 260°C, and 340°C, respectively, to determine the HC adsorption profile against the inlet gas temperature.

After each time HC adsorption was tested, the sample was calcined at 500°C to assure complete HC desorption.

Either toluene, representing the large HC molecule species, or propylene, representing the small HC molecule species, of the engine exhaust hydrocarbons, was used as the HC source gas for the simulated gas mixture.

### II-2) FTP TEST ON A MY96 3.8LITER VEHICLE

#### i) Sample Preparation:

FTP test samples (ADS-AX, ADS-A) were prepared by washcoating the Zeolite-AX or Zeolite-A and Pd catalyst onto cordierite honeycomb substrates. The Pd catalyst function was to oxidize the adsorbed HCs as they desorbed. The sample dimensions were 118mm $\phi$  • 200mm<sup>2</sup>. A reference sample (ADS-REF) was also prepared by coating nothing but the Pd catalyst onto the same contour substrates. In addition, Pd/Rh light-off catalyst (LO-1) and Pd light-off catalyst (LO-2) were also prepared as other major system components. Details of respective component samples are shown in Table 3.

Table 3. Component Parameters of the In-line HC Adsorber System

	Major Components				
	LO-1	LO-2	ADS-AX	ADS-A	ADS-REF
Dimensions:					
Wall Thickness [mm]	0.1	0.1	0.15	—	—
Cell Density [cells/cm <sup>2</sup> ] (mil/cpsi)	62 (4/400)	62 (4/400)	62 (4/400)	—	—
Substrates:					
Diameter [mm]	63	106	118	—	—
[inch]	(3.66)	(4.19)	(4.68)	—	—
Volume [liter]	0.0	1.2	1.072psi	—	—
Coating:					
Zeolite	—	—	Zeolite-AX	Zeolite-A	—
Zeolite Loading [g/liter]	0	0	160	100	0
Catalyst	Pd/Rh	Pd	Pd	Pd	Pd
PM Loading [g/liter] (g/cc)	6.98/0.25 (1827)	7.07 (200)	4.24 (120)	4.24 (120)	4.24 (120)

## ii) Accelerated Engine Aging:

The prepared HC adsorber samples were engine aged under the same accelerated engine aging conditions as shown in Table 1, except for the temperature conditions. In the case of these full-size samples, the bed temperatures were controlled to 550°C, 600°C, 650°C, 700°C, and 750°C, respectively. The varied temperatures were selected for the sake of more detailed investigation than the laboratory adsorption test, in which the aging temperature was either 650°C or 700°C.

Independent of the HC adsorbers, the LO-1 and LO-2 catalysts were also engine aged under the conditions which were regarded as equivalent to 50,000 vehicle miles in the under-floor position.

## iii) FTP Test:

After the engine dyno aging, the in-line HC adsorber system was installed in the under-floor position on a MY95 Buick LeSabre (3.8 liter, V6 engine). FTP emission tests were then carried out using Japanese domestic fuel. The FTP test configuration is illustrated in Figure 3.

Secondary air was not injected for all the FTP tests presented in this paper.

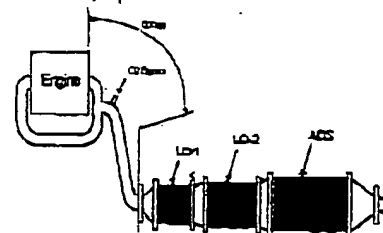


Figure 3. Illustration of FTP Test Configuration on MY95 Buick "LeSabre"

## III) TEST RESULTS

### III-1) LABORATORY ADSORPTION TEST

Figure 4 compares the correlation between the measuring temperature and the amount of adsorbed HCs for fresh samples which were coated with Zeolite-AX and Zeolite-A, respectively. Figure 4a shows the test results for toluene as the HC source, and Figure 4b for propylene.

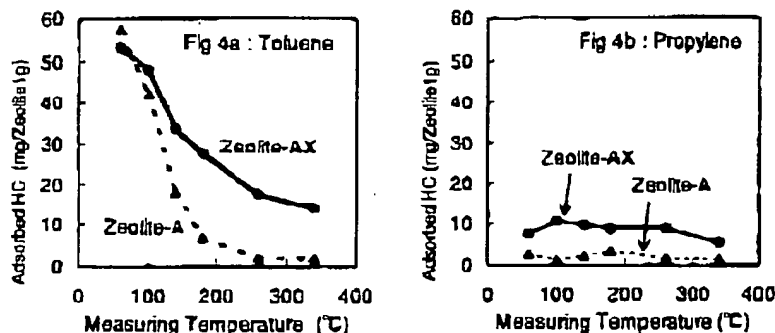


Figure 4. Measuring Temperature Dependency of HC Adsorption

The amounts of toluene adsorbed by Zeolite-AX and Zeolite-A samples were almost the same at temperatures below 100°C.

On the other hand, as shown in Figure 4b, the propylene adsorbed by Zeolite-A was minimal, however, Zeolite-AX exhibited a limited capability to adsorb propylene, even in aqueous conditions. The hypothesis is due to the chemical adsorption sites of Zeolite-AX.

The zeolite modifications resulting from additive X allowed for the adsorption of not only large HC molecules (toluene) but also fine HC molecules (propylene), whereas Zeolite-A's performance was limited to physically adsorbing large HC molecules due to the appropriate affinity between the originally large pore structure and the large HC molecules.

It was demonstrated that Zeolite-AX maintains its HC adsorption capability up to 350°C. As the physical adsorption limit of HC molecules by a zeolite material is generally understood to be around 100 to 150°C, we determined that the adsorption capability demonstrated at

these high temperatures supports the existence of chemical adsorption.

For example, in the case of toluene adsorption, Zeolite-AX, exhibiting a decrease in physical adsorption as the temperature increased from 100°C to 180°C, retained a certain amount of adsorption up to 350°C, which was considered to represent the chemisorption. On the other hand, Zeolite-A, which has only physical adsorption capability, depleted all of its adsorption capacity between 100°C and 180°C.

Next, we carried out a preliminary study on the thermal durability of the chemical adsorption sites.

Figure 5 plotted the amounts of toluene and propylene adsorbed by the Zeolite-AX and Zeolite-A samples, respectively, against the "fresh" and each engine aging temperature (600°C and 750°C). The data measured at the inlet gas temperatures of 100°C and 260°C were selected because these temperatures represented the following adsorption forms: both physical and chemical adsorptions could occur at 100°C, and only chemical adsorption occurred at 260°C.

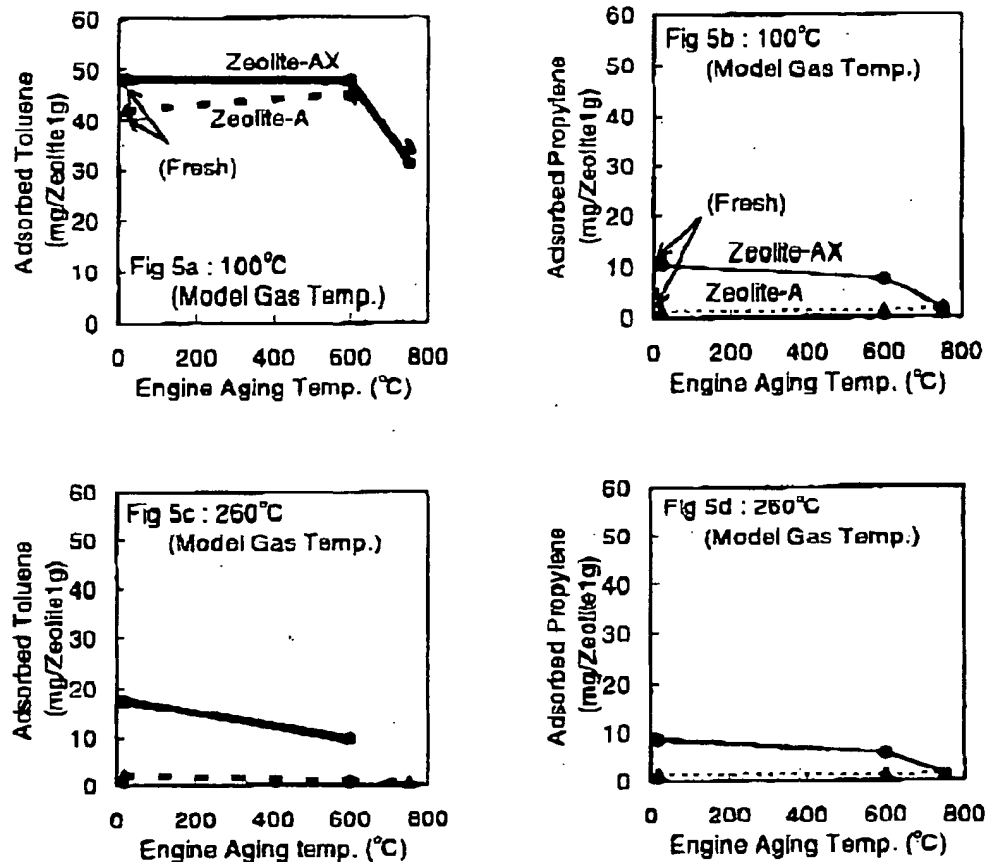


Figure 5. Engine Aging Temperature Dependency of HC Adsorption

Most of toluene adsorption by Zeolite-A at 100°C was found to remain even after engine aging at 750°C (Figure 5a). As the adsorption is physical, the pore structure of the Zeolite-A seems to have been primarily maintained up to 750°C. On the other hand, the propylene adsorption at inlet gas temperatures of 100°C (Figure 5b) and 260°C (Figure 5d) and toluene adsorption at 260°C (Figure 5c) by Zeolite-AX are considered to be chemical adsorption. From the fact that the chemical adsorption capability was maintained after engine aging at 600°C and lost at 750°C, the thermal stability limit of the chemical adsorption sites of Zeolite-AX was estimated to be between 600 to 750°C in this laboratory test.

### III-2) FTP TEST ON A MY95 3.8LITER VEHICLE

The laboratory adsorption test results proved not only the advantageous features of Zeolite-AX, previously described, but also highlighted our concern about its thermal stability. Therefore, the engine aging of full-size adsorber samples were conducted with more variation of temperatures around 600°C and 750°C, and furthermore, the system configuration

shown in Figure 3 was adopted. This configuration allowed the adsorber portion of the system to be installed as far as possible from the engine and heat sinks (i.e. : LO-1, LO-2 and supporting components) to be located between the engine and the adsorber. For all the FTP tests presented in this paper, LO-1 and LO-2 aged equivalent to 50,000 vehicle miles were used.

Figure 6 indicates the continuous HC concentration emitted from the tail pipe during the FTP tests carried out on the vehicle equipped with the In-line HC adsorber system having the ADS-AX and ADS-A, respectively, as an adsorber. All of the adsorber samples were "fresh". For reference, the HC concentration monitored at the outlet of the LO-2 and the ADS mid-bed temperature are also shown in the figure.

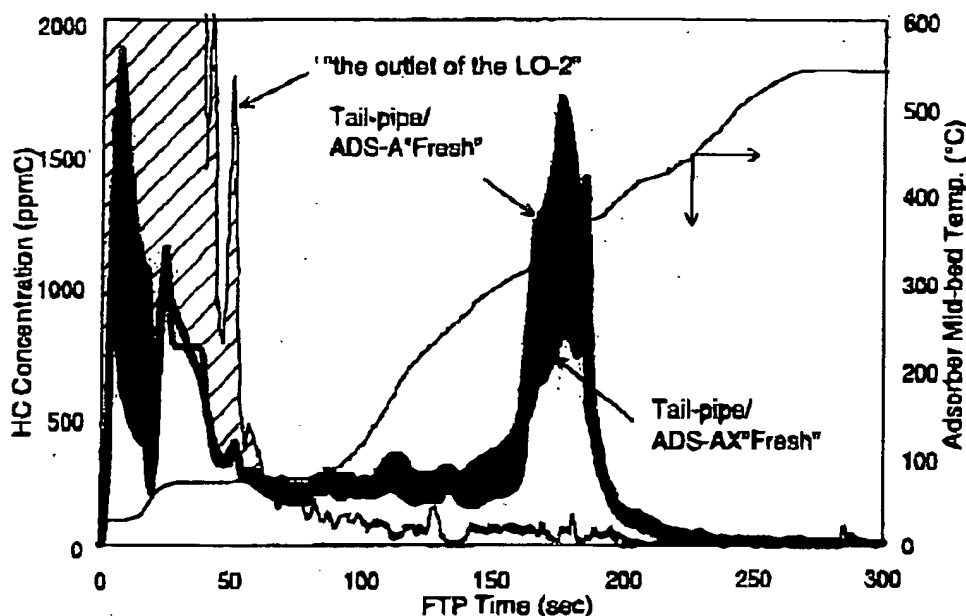


Figure 6. Continuous HC Concentration during Cold Start in FTP Tests

The difference in HC emission concentrations between "the outlet of the LO-2" and the ADS-A system just after the cold start (the dash-lined area) is considered to be the representation of physical adsorption of large HC molecules in the engine exhaust gas. In the case of the physical adsorption, the adsorption capability is lost at temperatures of 100 to 150°C, as previously explained. Therefore, most of the adsorbed HC molecules are released without being oxidized, because the coexisting catalyst components have not reached their activation temperature.

The difference between ADS-A system and ADS-AX system (the black area) can be attributed to the effects of the chemical adsorption property of the Zeolite-AX. These FTP test results confirm what had previously been indicated in the laboratory adsorption test.

In detail, the FTP test results of the ADS-AX can be analyzed as follows:

At the early stage of the cold start, HC adsorption efficiency was improved by adsorbing both large and fine HC molecules.

Also, since the chemical adsorption capability of the Zeolite-AX remained effective above 300°C, the coexisting catalyst components became active in time for desorption of the chemisorbed HCs to oxidize most of the desorbed HCs. Oxygen needed for the oxidation of the desorbed HCs seemed to be supplied by the  $\text{CeO}_2$  in the coexisting catalyst components.

In the next phase of evaluation, the thermal stability of chemical adsorption sites, which was identified as a concern for Zeolite-AX in the laboratory adsorption tests, was further investigated on the vehicle FTP tests. Table 4 shows the FTP test results for In-line HC adsorber systems comprised of the aged ADS-AX, ADS-A, and ADS-REF samples in addition to "fresh" samples, respectively. The data in this table indicate Bag1 HC emissions, because Bag1 represents the cold start stage in which HC adsorbers primarily demonstrate their HC adsorbing functions.

Figure 7 is a graph of the Table 4 data for ADS-AX and ADS-A.

Table 4. The Influence of Adsorber Aging Temperature on Bag1 HC Emission

ADS Aging Temp. (°C)	( Fresh )	550	600	650	700	750
ADS Sample						
ADS-AX	0.151	0.148	0.15	0.176	0.185	0.205
ADS-A	0.220	No Data	No Data	0.238	0.239	0.251
ADS-REF	No Data	No Data	No Data	0.237	No Data	No Data



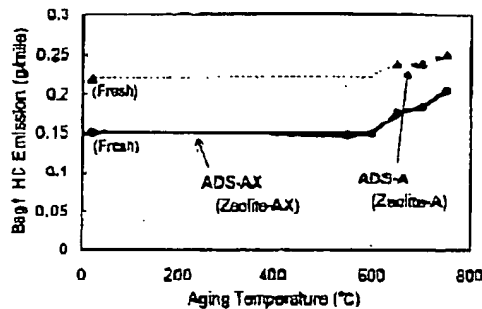


Figure 7. Effect of Engine Aging Temperature on Bag1 HC Emission

ADS-A exhibits the same Bag1 HC emission as that of ADS-REF after the engine aging at 650°C, a result of the ADS-A releasing most of the adsorbed HCs without oxidation. On the other hand, ADS-AX demonstrated a lower HC emission level in these FTP tests than that of the ADS-A, proving its advantage even after the engine aging at 750°C.

When we focus on the ADS-A first, the Bag1 HC emissions slightly increased from 650°C to 750°C. We attributed the slight increase to not the destruction of zeolite pore structures but the deterioration of the coexisting catalyst components. The pore structure of Zeolite-A was not significantly damaged by exposure to the temperatures up to 750°C, retaining most of its physical adsorption capability. This condition was supported by examination of the HC emission concentration profiles during the early stage (0-25 seconds) of the cold start (Figure 8). When comparing the HC profile of the 750°C aged ADS-A with the one of the "fresh" ADS-A, no significant difference was observed. During this cold start period the catalyst components are inactive, therefore, the no significant difference between them indicates the adsorbability of both aged and "fresh" Zeolite-A was equivalent.

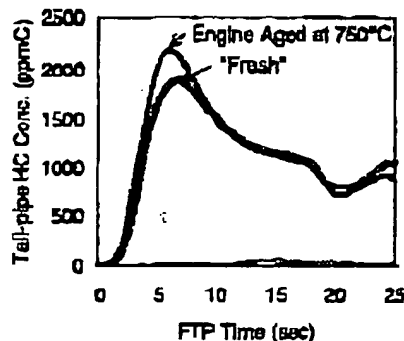


Figure 8. Continuous HC Concentration for ADS-A in Early Stage of Cold Start

Though ADS-A aged below 650°C was not tested, it is estimated to exhibit the same Bag1 HC emission as the "fresh" ADS-A, as was actually demonstrated by ADS-AX, which has the same zeolite pore structure as the ADS-A.

On the other hand, as demonstrated in the laboratory adsorption test results, the Bag1 HC emission of the ADS-AX increased gradually when aged above 600°C. Figure 9, which exhibits the HC emission concentration profiles of "fresh" and aged ADS-AX in the same manner as Figure 8 for ADS-A, also proves that Zeolite-AX gradually reduces its HC adsorption capability. This reduction in HC adsorption is believed to be caused by the partial deterioration of the chemical adsorption sites due to the cohesion of the X component above 650°C. With only the physical adsorption capability remaining, the HC emissions for Zeolite-AX seem to be converging to those for Zeolite-A at around 800 to 850°C. However, as mentioned above, the In-line HC adsorber system using the ADS-AX component actually provided an advantage over the ADS-A system up to 700 or 750°C as well as the ADS-REF system without any zeolite and the OEM converter aged under the same conditions as the LO-1 and LO-2 catalysts (Bag1 HC emission : 0.406g/mile) in FTP testing. Therefore, it would positively contribute to the reduction of HC emissions by arranging a better system layout with a lower exhaust heat load (e.g., positioning of the adsorbent downstream of the exhaust after-treatment system, placing a heat sink in front of the adsorber, etc.)

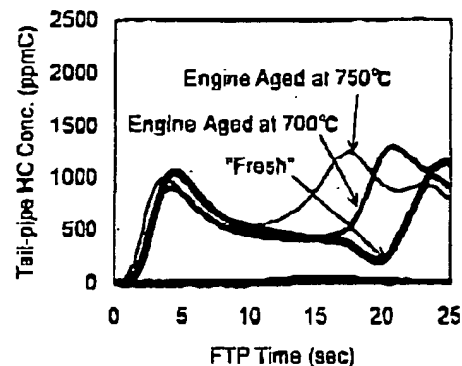


Figure 9. Continuous HC Concentration for ADS-AX in Early Stage of Cold Start

## IV) SUMMARY

1. Compared to the conventional adsorbent material (Zeolite-A), which provides only physical adsorption, using a unique adsorbent (Zeolite-AX), which can adsorb fine HC molecules even in the presence of water and also have a relatively high HC desorption temperature due to the effect of the chemical adsorption sites, allows significantly more HC emissions to be adsorbed for longer periods of time during the engine cold start. As a result, Bag1 HC emission level can be considerably reduced (for fresh adsorber : 31%, for 750°C aged adsorber : 18% reduction from ADS-A).
2. Although the thermal stability of the chemical adsorption sites of Zeolite-AX is a concern, the obvious Bag1 HC emission advantage of Zeolite-AX over Zeolite-A was maintained up to 750°C in the FTP tests.

## FUTURE STUDIES

The future studies we will conduct are:

- Study on the limits of the thermal stability of Zeolite-AX over Zeolite-A in vehicle tests
- Devise a passive system layout that can protect Zeolite-AX from extreme exhaust heat
- Study of the thermal stability of Zeolite-AX at higher temperatures but for shorter time in view of possible engine malfunctions
- Combination of the Zeolite-AX adsorber with other exhaust gas purification technologies (e.g. low temperature light-off catalyst material, thin wall substrates, and EHC)
- Determine HC storage capacity of Zeolite-AX adsorber (i.e. Determine the number of FTP cold starts before Zeolite-AX adsorber is saturated)
- Determine the effects of sulfur on HC adsorber performance

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